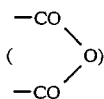


ADHESIVE COATING MATERIAL

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to an adhesive coating material for a hard tissue, which comprises a specific polymer and a specific compound in combination. More particularly, the present invention relates to an adhesive coating material for a hard tissue, which comprises (1) a polymer having an acid value of 30 to 700 and including in recurring units a hydrophobic group and two carboxyl ($-\text{COOH}$) groups or one carboxylic anhydride



group bonded to the polymer, said carboxyl groups or carboxylic anhydride group being bonded to adjacent carbon atoms, and (2) a polymerizable vinyl compound or a mixture of said polymerizable vinyl compound acid and an organic titanate compound.

(2) Description of the Prior Art

Various compounds are known as adhesives applicable peculiarly in various fields. Among these adhesives, especially severe requirements are imposed on dental adhesives used to hard tissues in humid condition. Since a dental adhesive is used in the oral cavity, a high adhesion strength in the humid condition is required. Furthermore, this dental adhesive should have an adhesive force to both of hard tissue and a dental resinous restorative material comprising a polymerizable monomer and at least one member selected from inorganic, organic and inorganic/organic composite fillers.

As dental adhesives, Ionomer cement comprising an aqueous solution of polyacrylic acid and inorganic oxide, and a cold-setting adhesive comprising a polymerizable monomer are widely used.

The Ionomer cement has an adhesive force to the hard tissue, but no adhesive force to a dental resinous restorative material. And the Ionomer cement is readily separated from the bonded portion since its water resistance is low.

The cold-setting adhesive comprising a polymerizable monomer hardly adheres to the hard tissue without pretreatment. Accordingly, it is necessary that the hard tissue should be treated with a highly concentrated aqueous solution of phosphoric acid to prepare a mechanical retentive surface. This method, however, is defective in that even healthy hard tissue is damaged since phosphoric acid is used at a high concentration.

Special properties are required for adhesives according to their specific applications, and an adhesive usable in a certain field can seldom be used industrially in other fields. Accordingly, special adhesives are used in respective application fields, and also in the field of the dental treatment, development of an adhesive satisfying the foregoing requirements is eagerly desired.

SUMMARY OF THE INVENTION

Under the above-mentioned background, we carried out research with a view to developing a satisfactory adhesive coating material for a hard tissue, and we have now completed the present invention.

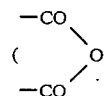
It is therefore a primary object of the present invention to provide an adhesive for a hard tissue, which can

be bonded to a hard tissue directly without a pretreatment with an aqueous solution of phosphoric acid.

Another object of the present invention is to provide an adhesive which can be bonded with a sufficient adhesive force to a tooth and a dental resinous restorative material even in the mouth cavity in the humid condition and which was a high water resistance.

Other objects and advantages will become apparent from the description given hereinafter.

In accordance with a fundamental aspect of the present invention, there is provided an adhesive coating material for a hard tissue, which comprises (1) a polymer having an acid value of 30 to 700 and including in recurring units a hydrophobic group and two carboxyl ($-\text{COOH}$) groups or one carboxylic anhydride



group bonded to the polymer, said carboxyl groups or carboxylic anhydride group being bonded to adjacent carbon atoms, and (2) a polymerizable vinyl compound or a mixture of said polymerizable vinyl compound and an organic titanate compound.

DETAILED DESCRIPTION OF THE INVENTION

One main component of the adhesive coating material of the present invention is a polymer including in recurring units a hydrophobic group and two carboxyl groups or one carboxylic anhydride group bonded to the polymer, said carboxyl groups or carboxylic anhydride group being bonded to adjacent carbon atoms. The reason why the hydrophobic group is introduced into the polymer used in the present invention is that a sufficient water resistance is given to the adhesive coating material, a good compatibility or affinity with a resin to be bonded, for example, a dental resinous restorative material, is imparted to the adhesive coating material and a sufficient adhesion strength is obtained even in the humid condition. Furthermore, in order to attain a sufficient adhesive strength to the hard tissue even in the humid condition, it is necessary that the two carboxyl groups or one carboxylic anhydride group should be bonded to adjacent carbon atoms in the polymer to be used in the present invention. Since the two carboxyl groups or one carboxylic anhydride group forms a bridge of a high strength with the organic titanate compound used as the other component of the present invention, an especially high water resistance is given to the adhesive coating material of the present invention. Moreover, in the adhesive coating material of the present invention, since the polymerizable vinyl monomer is polymerized in the state where the coating material is uniformly impregnated with the polymerizable vinyl compound, the adhesion strength of the adhesive coating material of the present invention is highly improved. Accordingly, the adhesive coating material of the present invention acts effectively as an adhesive between a hard tissue and a dental resinous restorative material such as a composite resin, especially in the humid condition. In view of the foregoing description, it is most preferred that the adhesive coating material of the present invention should comprise (1) a polymer including a hydrophobic group and two carboxyl